Comparison of Density Functionals for Reactions of Sulfur Ylides with Aldehydes and Olefins

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The reactions of a model sulfur ylide with formaldehyde and 1,1-dicianoethylene, leading to the formation of an epoxyde and a cyclopropane, respectively, have been studied using different computational methods, and the results have been compared to those obtained with the CBS-QB3 method. The second step of these reactions presents transition states similar to that of an S_N2 reaction. Depending on the degree of electron delocalization at the transition state, a different amount of exact exchange is necessary in the exchange functional to obtain accurate energy barriers. This amount is larger for the reaction of formaldehyde, in which the transition state is more delocalized, than for the reaction of 1,1-dicianoethylene. Similar results have been obtained for symmetric and non-symmetric S_N2 reactions. The calculation of the reaction path has shown that the error relative to CBS-QB3 tends to increase when approaching the transition state. Among the different computational methods, PBE1PBE is the one to provide the most accurate energy barriers and reaction energies, whereas BB1K leads to the best results for the reaction path before the transition state.

Introduction

The Kohn−Sham density functional theory (DFT)[1−3] is the most widely used method for computational and theoretical chemists. The key to its success has been its capacity to predict important aspects of a large range of chemical systems with a low computational cost in comparison with post-Hartree−Fock methods.

The development of new exchange-correlation functionals has allowed the use of DFT in the study of chemical reactivity. In particular, hybrid functionals, such as B3LYP,[4,5] have successfully been used for many chemical reactions.[3d,6−13] However, there are certain types of reactions in which the most popular DFT methods present failures. For instance, it is well-known that GGA and B3LYP functionals tend to understimate barriers for S_N2 reactions.[14−30]

The failure of GGA functionals in the study of symmetric S_N2 reactions has been related to the tendency of these functionals to overestimate the stability of delocalized structures such as the transition state of S_N2 reactions,[17] which involve two electron pairs delocalized over three centers (see Scheme 1).

The use of hybrid exchange functionals, which include a certain amount of exact exchange, partially corrects this error. However, the amount of exact exchange necessary to obtain accurate results is larger than for other kinds of reactions.

The addition of sulfur ylides to aldehydes or olefins, provide an attractive path in the syntheses of epoxides (see Scheme 2) or cyclopropanes (see Scheme 3), respectively. In the last years, several theoretical studies of these reactions using DFT methods have been reported.[31−36]

These reactions take place in two steps, through the formation of betaine intermediates. The second step involves the formation of a C−O or a C−C bond along with the elimination of a thioether. The transition state of this second step has similarities
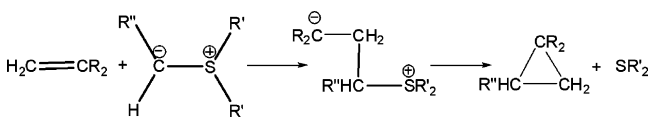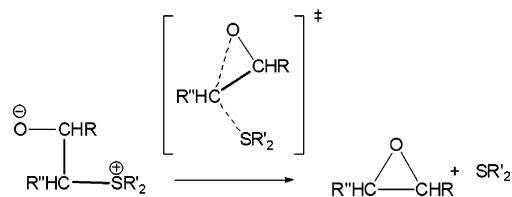
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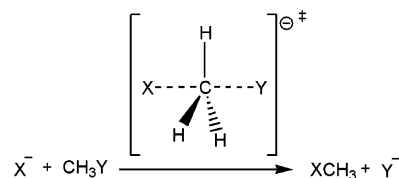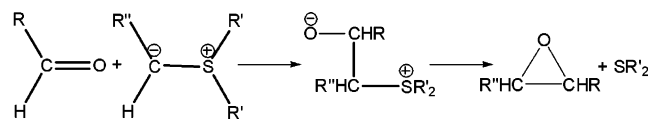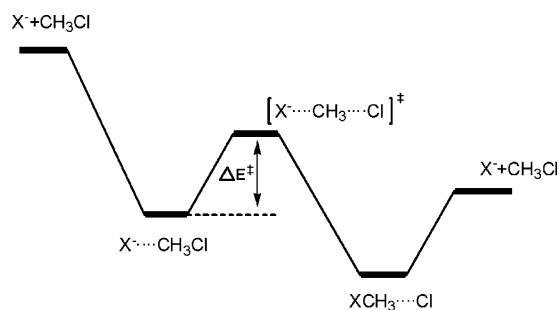
SCHEME 1

SCHEME 2

SCHEME 3

SCHEME 4

with that of an S_N2 reaction, since it involves two electron pairs delocalized over three centers (see Scheme 4). So, this step may be subject to the same problems as S_N2 reactions.

Thus, we have decided to study the reactions of a model sulfur ylide with formaldehyde and with 1,1-dicianoethylene using different DFT functionals and to compare the results with those provided by the multi-level CBS-QB3 method.[37] The same methods have also been used in the study of a symmetric and several non-symmetric S_N2 reactions.

Figure 1. Schematic potential energy profile of the S_N2 reaction between X^- and CH_3Cl.

Computational Details

The structures of all stationary points of the studied reactions have been computed using the CBS-QB3 method.[37] It involves a geometry optimization and frequency calculation at the B3LYP/6-311G(d,p) level of theory and then single point calculations with CCSD(T),[38] MP4SDQ,[39] and MP2[40] methods, including an extrapolation to complete the basis set at the MP2 level. This method has already been used as a reference in the study of different kinds of chemical reactions.[13,18,26,41–46] A comparison of the performance of the CBS-QB3 method and other multilevel methods in the computation of potential energy barriers can be found in ref 47.

For the stationary points obtained at the CBS-QB3 level, we have done single point calculations using different density functionals with the 6-311++G(2df,2pd) basis set. We have used 12 density functionals, which may be divided into GGA, meta-GGA, and hybrid functionals. The GGA functionals are BLYP,[5,48] OLYP,[5,49] PBEPBE,[50,51] OPBE,[49–51] and HCTH/407.[52,53] As the meta-GGA functional, we have chosen TPSSTPSS.[54] Finally, we have used the hybrid functionals B3LYP, BHandHLYP,[5,48,55] PBE1PBE,[50,51,56] BB1K,[48,57,58] TPSSh,[59] and M05-2X.[60] We have also done single point calculations at the MP2/6-311++G(2df,2pd) level of calculation.

For the second step of the epoxydation and cyclopropanation reactions, we have computed the intrinsic reaction coordinate (IRC)[61,62] at the B3LYP/6-311G(d,p) level and recalculated selected points along the reaction path with different theoretical methods.

Calculations have been carried out with the Gaussian-03 program,[63] with the exception of those involving the M05-2X

functional, which have been done with a modified version of the NWChem package.[64]

Results and Discussion

Before studying the target reactions, we have examined the behavior of the different density functionals in the study of several S_N2 reactions, and their results will be presented first.

S_N2 Reactions. We have studied the reactions of CH_3Cl with Cl^-, F^-, HS^-, and N_3^-. Figure 1 shows the schematic energy profile for a S_N2 reaction. For all reactions, we have computed the central energy barrier ($\Delta E^\ddagger$), and the results obtained with different methods are shown in Table 1. The geometries have been optimized using the 6-31+G(d,p), since the inclusion of diffuse functions is necessary to locate the transition states of the non-symmetrical reactions. The potential energy barriers at different stages of the CBS-QB3 calculation can be found as Supporting Information.

The results obtained for the reactions of Cl^- and F^- may be compared with the CCSD(T) energy barriers compiled by Swart et al.[29] These barriers are in the 12.9–13.5 kcal mol^{-1} range for the symmetric reaction and between 2.0 and 3.7 kcal mol^{-1} for the F^- reaction. The CBS-QB3 results shown in Table 1 lie within these ranges. On the other hand, Parthiban et al.[18] have computed the barriers for these two reactions using the W1′ method, and their results show that the CBS-QB3 method may underestimate the energy barriers by 0.5–0.6 kcal mol^{-1}. For the symmetric reaction, we have also calculated the potential energy barrier at the CCSD(T) level of calculation using Dunning correlation consistent basis sets up to cc-pVQZ[65] and aug-cc-pVTZ[66] to extrapolate to the basis set limit.[67] The obtained potential energy barriers are 13.1 and 13.2 kcal mol^{-1}, respectively, in excellent agreement with the CBS-QB3 value.

If we take the CBS-QB3 results as a reference, then Table 1 shows that the best results are obtained with the hybrid functionals, which include the largest amount of exact exchange: BB1K (42%), BHandHLYP (50%), and M05-2X (56%). For the first two functionals, the mean unsigned error (MUE) is clearly lower than 1 kcal mol^{-1}, whereas for M05-2X, it is 1 kcal mol^{-1}. Notice the good behavior of OPBE, which is the best local GGA functional,[24] and of PBE1PBE (only 25% of exact exchange). Taking into account that the CBS-QB3 barriers may be slightly underestimated,[18] BB1K is probably the functional that provides the most accurate results.

The symmetric reaction is the one that requires the largest amount of exact exchange to yield reasonable results. On the

TABLE 1: Potential Energy Barriers^a for S_N2 Reactions between X^- and CH_3CL Computed with Different Methods^b

method	Cl		F		HS		N$_3$		M.U.E.^{c}
CBS-QB3	13.1	(0.0)	2.3	(0.0)	8.0	(0.0)	11.5	(0.0)	0.0
BLYP	5.3	(−7.8)	−1.0	(−3.3)	1.0	(−7.0)	4.9	(−6.6)	6.2
B3LYP	8.8	(−4.3)	0.4	(−1.9)	4.2	(−3.8)	8.2	(−3.3)	3.3
BB1K	13.5	(+0.4)	2.5	(+0.2)	8.4	(+0.4)	12.7	(+1.2)	0.6
BHandHLYP	12.6	(−0.5)	2.0	(−0.3)	8.0	(0.0)	11.8	(+0.3)	0.3
OLYP	9.6	(−3.5)	0.8	(−1.5)	4.7	(−3.3)	9.3	(−2.2)	2.6
OPBE	11.3	(−1.8)	1.6	(−0.7)	6.1	(−1.9)	11.0	(−0.5)	1.2
PBEPBE	7.0	(−6.1)	−0.2	(−2.5)	2.4	(−5.6)	6.2	(−5.3)	4.9
PBE1PBE	11.1	(−2.0)	1.5	(−0.8)	6.2	(−1.8)	10.3	(−1.2)	1.5
TPSSTPSS	5.4	(−7.6)	−1.3	(−3.6)	1.2	(−6.8)	4.6	(−6.9)	6.2
TPSSh	7.2	(−5.9)	−0.5	(−2.8)	2.9	(−5.1)	6.4	(−5.1)	4.7
HCTH/407	10.0	(−3.1)	1.0	(−1.3)	5.3	(−2.7)	9.4	(−2.1)	2.3
M05-2X	11.7	(−1.4)	1.7	(−0.6)	6.8	(−1.2)	10.6	(−0.9)	1.0
MP2	15.1	(+2.0)	3.6	(+1.3)	9.7	(+1.7)	14.2	(+2.7)	1.9

^{a} In kcal mol^{-1}. In parentheses error with respect to CBS-QB3. ^{b} B3LYP/6-31+G(d,p) geometries. ^{c} Mean unsigned error relative to CBS-QB3 in kcal mol^{-1}.

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TABLE 2: Geometry Parameters,[a] Bond Indices, and Localization Index for Transition States of CH₃Cl + X⁻ Sₙ2 Reactions

X	R_{X-C}	R_{C-Cl}	B_{X-C}	B_{C-Cl}	α
Cl	2.36	2.36	0.48	0.48	0.00
F	2.15	2.10	0.32	0.64	0.33
HS	2.62	2.23	0.43	0.55	0.13
N₃	2.13	2.29	0.36	0.52	0.18

[a] Interatomic distances in Å.

SCHEME 5

Z= O, C(CN)₂
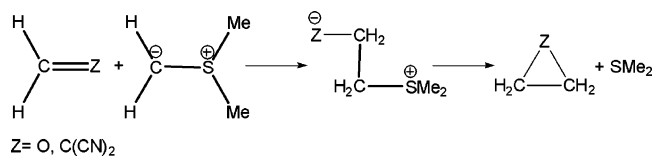
other hand, for the non-symmetric reactions the amount of exact exchange necessary varies from one case to another. This fact is closely related to the degree of electron delocalization at the transition state. With the purpose of quantifying the transition state delocalization, we may define a localization index, α, computed from the C−Cl and X−C Wiberg bond indexes,[68] B_i, evaluated using the Natural Bond Orbital Method (NBO)[69] at the transition state.

$$\alpha = \frac{B_{C-Cl} - B_{X-C}}{B_{C-Cl} + B_{X-C}} \tag{1}$$

Table 2 presents the most relevant geometry parameters, the bond indices, and the localization index for the four transition states. For the symmetric reaction, in which the transition state is synchronous, errors lower than 1 kcal mol⁻¹ are obtained only with the BHandHLYP or BB1K functionals, which include at least a 42% exact exchange.

Alternatively, for the reaction with F⁻, which presents the most localized transition state, PBE1PBE (25% exact exchange) or even OPBE (a pure GGA functional) provide energy barriers with an error lower than 1 kcal mol⁻¹. However, this reaction has the lowest energy barrier, and an error of 1 kcal mol⁻¹ corresponds to 43% of the CBS-QB3 barrier. The reaction with N₃⁻ has the second most localized transition state ($\alpha = 0.18$) and presents an energy barrier similar to the symmetric reaction. In this case, OPBE and PBE1PBE also present relatively low errors.

The study of these Sₙ2 reactions is only a previous step in the study of sulfur ylide reactions with formaldehyde and 1,1-dicianoethylene, which have been studied using the same methodology as the Sₙ2 reactions.

Reactions of Sulfur Ylide with Formaldehyde and 1,1-Dicianoethylene. We have studied the reactions of the model sulfur ylide (CH₃)₂S═CH₂ with formaldehyde and 1,1-diciano-ethylene. The first step of the reaction involves the formation of a betaine intermediate (see Scheme 5).

There are two different betaine conformers, anti and gauche, but in the gas phase only the gauche conformer is a minimum of the potential energy surface. For this reason, we have only considered the gauche conformers and their evolution to either epoxide or cyclopropane.

Figure 2 shows the potential energy diagram for the whole process. A schematic representation of the transition states corresponding to the second step is shown in Figure 3. The reaction energies and potential energy barriers computed with
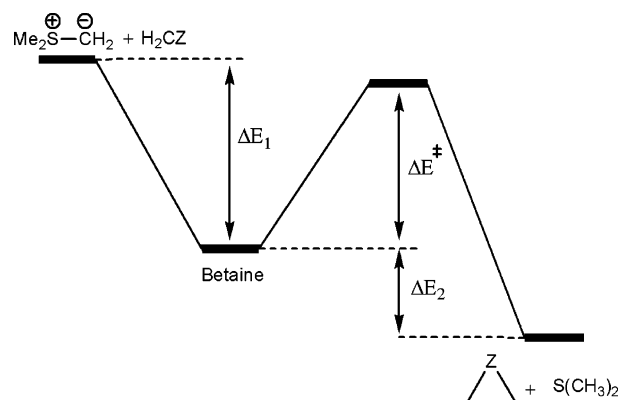
Figure 2. Schematic potential energy diagram for reactions of a sulfur ylide with formaldehyde (Z═O) and 1,2-dicianoethylene (Z═C(CN)₂).
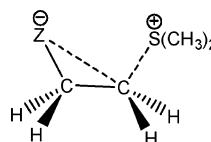
Figure 3. Schematic representation of the transition state corresponding to the epoxidation (Z═O) or cyclopropanation (Z═C(CN)₂) reactions.

TABLE 3: Reaction Energies and Potential Energy Barrier[a] for the Reaction between Sulfur Ylide and Formaldehyde Computed with Different Methods[b]

method	ΔE_1		$\Delta E^{\ddagger}$		ΔE_2		M.U.E.[c]
CBS-QB3	−20.2	(0.0)	36.2	(0.0)	−13.9	(0.0)	0.0
BLYP	−11.3	(+9.1)	23.6	(−12.6)	−19.1	(−5.2)	9.0
B3LYP	−13.3	(+6.9)	29.7	(−6.6)	−20.2	(−6.3)	6.6
BB1K	−18.6	(+1.6)	37.9	(+1.7)	−20.8	(−6.9)	3.4
BHandHLYP	−14.2	(+6.0)	35.5	(−0.7)	−22.6	(−8.7)	5.1
OLYP	−9.9	(+14.8)	28.3	(−7.9)	−23.9	(−10.0)	10.9
OPBE	−15.9	(+4.3)	33.8	(−2.4)	−21.2	(−7.3)	4.7
PBEPBE	−20.9	(−0.7)	29.8	(−6.4)	−21.2	(−7.3)	2.9
PBE1PBE	−21.1	(−0.8)	36.1	(−0.1)	−15.7	(−1.8)	0.9
TPSSTPSS	−18.8	(+1.4)	28.0	(−8.2)	−17.6	(−3.7)	4.4
TPSSh	−18.9	(+1.3)	30.6	(−5.6)	−18.6	(−4.7)	3.8
HCTH/407	−10.6	(+9.7)	28.2	(−8.0)	−22.9	(−9.0)	8.9
M05-2X	−21.7	(−1.5)	38.7	(+2.5)	−16.3	(−2.4)	2.1
MP2	−21.0	(−0.8)	43.3	(+7.1)	−13.0	(+0.9)	2.9

[a] In kcal mol⁻¹. See Figure 3. In parentheses error with respect to CBS-QB3. [b] B3LYP/6-311G(d,p) geometries. [c] Mean unsigned error relative to CBS-QB3 in kcal mol⁻¹.

different methods for the epoxidation and cyclopropanation reactions are presented in Tables 3 and 4, respectively.

An examination of the results obtained for the reaction with formaldehyde (Table 3) shows that the methods which provide the best results for the formation energy of the betaine (ΔE_1) are PBEPBE, PBE1PBE, and MP2 (errors lower than 1 kcal mol⁻¹), and TPSSh, TPSSTPSS, M05-2X, and BB1K (errors between 1 and 2 kcal mol⁻¹). Among these methods, only PBE1PBE and BB1K yield potential energy barriers for the second step of the reaction that differ by less than 2 kcal mol⁻¹ with respect to the CBS-QB3 value. BHandHLYP also leads to an accurate energy barrier. With regard to the reaction energy of the second step (ΔE_2), the most accurate results (with an error less than 2 kcal mol⁻¹) are MP2, PBEPBE, and PBE1PBE. According to the mean errors between the three magnitudes, PBE1PBE yields the most accurate results, whereas M05-2X is the second most accurate method. However, if we are mainly interested in the potential energy barrier of the epoxide formation, then BHandHLYP and BB1K yield better results than those of M05-2X.

With regard to the reaction with 1,1-dicianoethylene (Table 4), we can observe that the only methods to predict the formation

TABLE 4: Reaction Energies and Potential Energy Barrier[a] for the Reaction between Sulfur Ylide and 1,1-dicianoethylene Computed with Different Methods[b]

method	ΔE_1		$\Delta E_n^{\ddagger}$		ΔE_2		M.U.E.[c]
CBS-QB3	−31.8	(0.0)	29.3	(0.0)	−16.2	(0.0)	0.0
BLYP	−21.1	(+10.7)	17.9	(−11.4)	−18.8	(−2.6)	8.2
B3LYP	−25.4	(+6.4)	24.3	(−5.0)	−19.5	(−3.3)	4.9
BB1K	−33.1	(−1.4)	32.2	(+2.9)	−20.0	(−3.8)	2.7
BHandHLYP	−29.0	(+2.8)	31.5	(+2.2)	−24.1	(−7.9)	4.3
OLYP	−20.0	(+11.8)	22.1	(−7.2)	−24.6	(−8.4)	9.1
OPBE	−27.0	(+4.8)	27.1	(−2.2)	−22.4	(−6.2)	13.2
PBEPBE	−32.2	(−0.5)	23.2	(−6.1)	−12.2	(+4.0)	3.5
PBE1PBE	−34.9	(−3.1)	30.1	(+0.8)	−15.2	(+1.0)	1.6
TPSSTPSS	−28.7	(+3.0)	21.8	(−7.5)	−17.2	(−1.0)	3.8
TPSSh	−30.0	(+1.8)	24.7	(−4.6)	−26.3	(−10.1)	5.5
HCTH/407	−22.4	(+9.4)	21.5	(−7.8)	−22.8	(+6.6)	7.9
M05-2X	−37.1	(−5.3)	32.1	(+2.8)	−13.9	(2.3)	3.4
MP2	−34.8	(−3.0)	37.4	(+8.1)	−15.1	(+1.1)	4.1

[a] In kcal mol^{-1}. See Figure 3. In parentheses, error with respect to CBS-QB3. [b] B3LYP/6-311G(d,p) geometries. [c] Mean unsigned error relative to CBS-QB3 in kcal mol^{-1}.
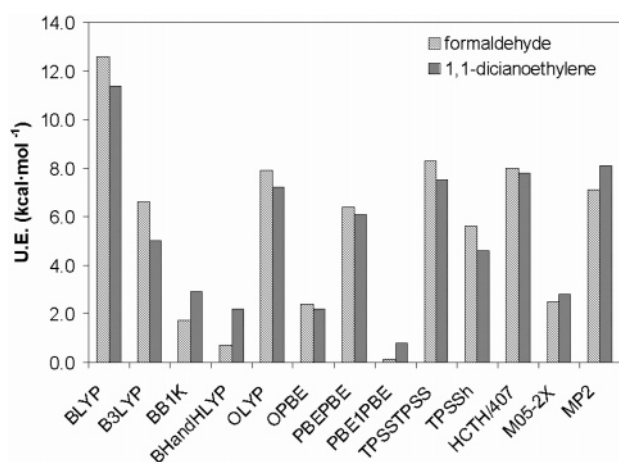
Figure 4. Comparison between unsigned errors relative to CBS-QB3 for energy barriers of the second step of reactions of sulfur ylide with formaldehyde and 1,1-dicianoethylene computed with different methods.

energy of the betaine with an accuracy of less than 2 kcal mol^{-1} are PBEPBE, BB1K, and TPSSh. The best result for the potential energy barrier is obtained with PBE1PBE, whereas for the reaction energy of the second step, PBE1PBE and TPSSTPSS yield the best results.

Let us focus our attention on the potential energy barrier of the second step of the reactions. A comparison of the unsigned errors for both reactions can be found in Figure 4. With B3LYP and GGA functionals, the error is larger for the epoxydation than for the cyclopropanation, whereas the situation is reversed for those hybrid funcionals with the largest amount of exact exchange (BB1K, BHandHLYP, and M05-2X) and for PBE1PBE.

This different behavior may be related to the different degree of electron delocalization at the transition states (see Figure 4), which can be measured from the localization index

$$\alpha = \frac{B_{S-C} - B_{C-X}}{B_{S-C} + B_{C-X}} \qquad (2)$$

computed from the bond indexes B_i at the transition state. The most relevant geometry parameters, bond indices and localization indices at the transition states are shown in Table 5. We observe that the transition state for the epoxydation reaction is more delocalized than that for the cyclopropanation reaction.

TABLE 5: Geometry Parameters,[a] Bond Indices, and Localization Index of Transition States for Reactions between Sulfur Ylide and Formaldehyde (X=O) or 1,1-Dicianoethylene (X=C(CN)$_2$)

X	R_{X-C}	R_{C-S}	B_{X-C}	B_{C-S}	α
O	2.09	2.51	0.41	0.44	0.03
C(CN)$_2$	2.33	2.56	0.28	0.44	0.22

[a] Interatomic distances in Å.

The hybrid functionals with the largest amount of exact exchange (BB1K, BHandHLYP, and M05-2X) perform better for the reaction with the most localized transitions state, whereas GGA functionals and B3LYP lead to better results for the reaction with delocalized a transition state. The PBE1PBE functional does not fit to this scheme, since with only a 25% of exact exchange leads to an excellent result for the epoxidation reaction.

For these reactions, we have varied the amount of exact exchange in the density functional from 0 to 70%, using the adiabatic connection method (eq 3) for the density functionals (DF) BLYP, PBEPBE, and BB95. This expression includes BHandHLYP ($a_1 = 0.5$), PBE1PBE ($a_1 = 0.25$), B1B95[45,54] ($a_1 = 0.28$), and BB1K ($a_1 = 0.42$).

$$E_{xc}^{ACM1} = E_{xc}^{DF} + a_1(E_x^{exact} - E_x^{DF}) \qquad (3)$$
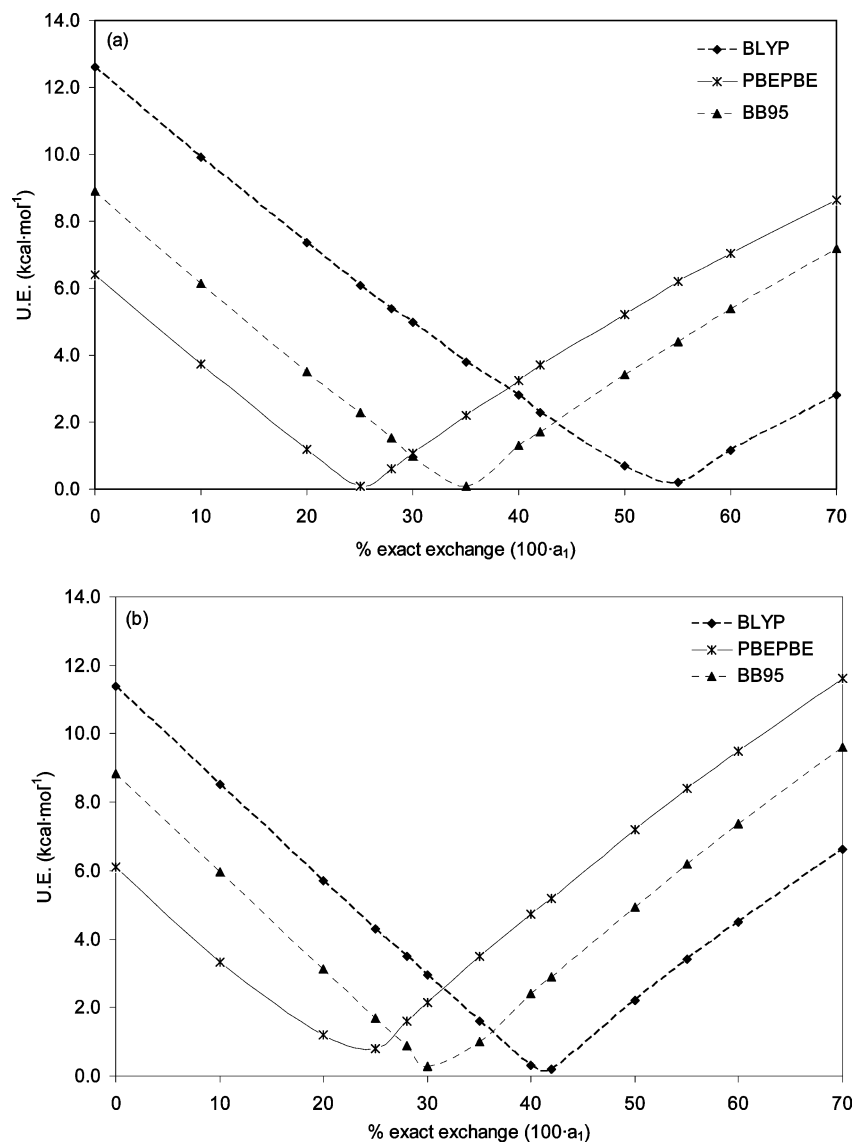
We have computed the potential energy barriers for the reactions and the unsigned error relative to the CBS-QB3 values. The results are shown in Figure 5.

For the BLYP functional, the amount of exact exchange necessary to achieve a certain accuracy (e.g., 1 kcal mol^{-1}) varies from one reaction to another by about 10%. In this way, the best result for the epoxidation reaction is obtained with about 55% exact exchange, whereas for the cyclopropanation reaction, a value slightly above 40% is enough.

In a recent work, Aggarwal et al.[34] have studied the reaction between benzaldehyde and an ammonium ylide at the B3LYP level of theory. For a model reaction, they have verified that the results obtained with B3LYP are comparable with those obtained with the G2 multilevel method.[70] The localization index at the transition state of their model reaction is 0.28, so that this transition state is more localized than the ones corresponding the model reactions above considered; and for this reason, the B3LYP functional yields an accurate potential energy barrier.

The BB95 functional requires less exact exchange than does BLYP. For the epoxidation reaction, the best result is obtained with 35% exact exchange, whereas for the cyclopropanation reaction, a value of 30% exact exchange is enough. These results are consistent with the fact that the more delocalized the transition state, the more exact exchange is necessary. Moreover, they also show that for the same exchange functional (Becke88), the amount of exact exchange necessary depends on the correlation functional (LYP or B95).

The results obtained for the PBEPBE functional show a lower variation from one reaction to another. Errors lower than 1 kcal mol^{-1} are obtained for 21% of exact exchange in the epoxydation reaction and 18% in the cyclopropanation. The minimum errors correspond to 25% and 22%, respectively. These results show that hybrid functionals based on PBEPBE with a given amount of exact exchange may lead to excellent results for both reactions, regardless of the degree of electron delocalization of their transition states. In particular, the PBE1PBE functional leads to the smallest mean unsigned error relative to CBS-QB3 for the energy barriers and reaction energies, as shown in Tables 3 and 4.

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Figure 5. Unsigned error relative to CBS-QB3 for the energy barrier of the second step of reactions of sulfur ylide with formaldehyde (a) and 1,1-dicianoethylene (b) computed with the BLYP, BB95, and PBEPBE functionals with different contributions of exact exchange.

Until now, we have focused our attention mainly on the potential energy barriers of the epoxide and cyclopropane formation steps. However, this provides only a first approach to the study of chemical reactivity. A second level of approximation would require the calculation of the complete reaction path. To compare the reaction paths obtained by different methods, we have calculated the IRC for both reactions at the B3LYP/6-311G(d,p) level of calculation, as it is the level at which geometries are optimized in the CBS-QB3 method. Figure 6 shows the variation of the localization index along the reaction paths of the two reactions.

For selected points of these IRCs, we have done single-point calculations of their energies using different computational methods. The complete results can be found in the Supporting Information.

Figure 7 shows the variation of the error with respect to the CBS-QB3 method along the reaction paths for selected density functionals. It can be observed that for both reactions, the BLYP and B3LYP functionals introduce large errors with respect to CBS-QB3. In both cases, the error increases in absolute value when approaching the transition state and reaches its maximum just before the transition state. For the other density functionals,
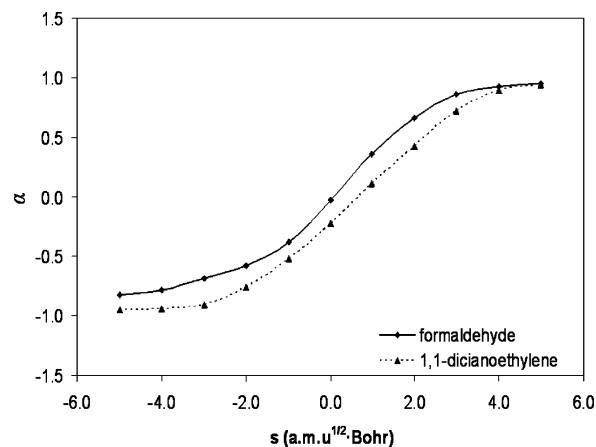
Figure 6. Variation of the localization index along the reaction path computed at the B3LYP/6-311G(d,p) level of calculation for the reactions of sulfur ylide with formaldehyde and 1,1-dicianoethylene. The position of the transition states correspond to $s = 0$.

the errors are much lower. In particular, BB1K provides the best description of the reaction path before the transition state.
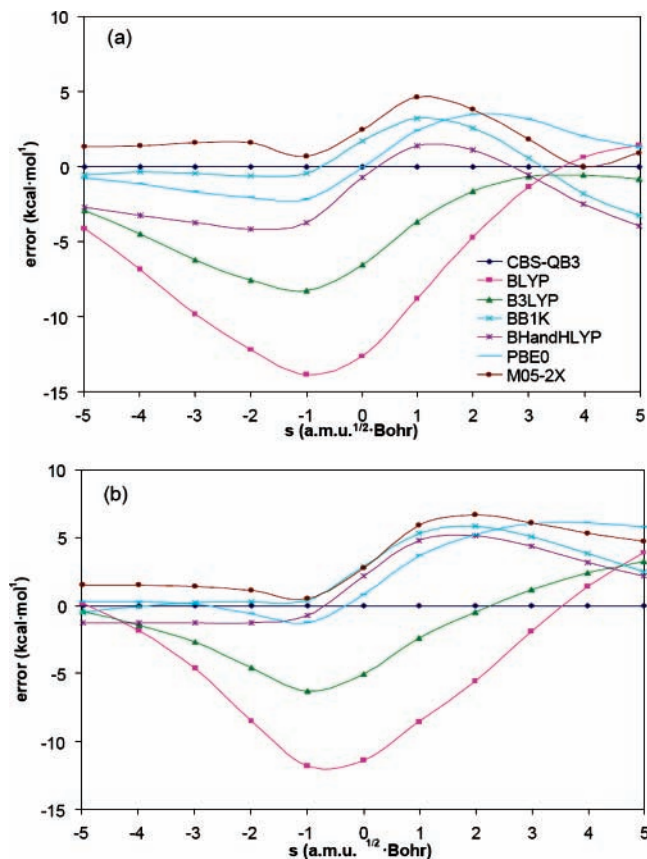
Figure 7. Error with respect to CBS-QB3 obtained with different methods for selected points along the reaction path of the reactions of sulfur ylide with formaldehyde (a) and 1,1-dicianoethylene (b).

Concluding Remarks

We have studied the reactions of a model sulfur ylide with formaldehyde and 1,1-dicianoethylene using different computational methods, and the results have been compared to those obtained with the CBS-QB3 method. Special attention has been paid to the second step of each reaction, which leads to the formation of an epoxyde and a cyclopropane, respectively, and present transition states similar to that of a S_N2 reaction.

Depending on the degree of electron delocalization at the transition state, measured from a localization index derived from bond indices, a different amount of exact exchange is necessary in the exchange functional to obtain accurate energy barriers. This amount is larger for the reaction of formaldehyde, where the transition state is more delocalized, than for the reaction of 1,1-dicianoethylene. Similar results have been obtained for a symmetric and a non-symmetric S_N2 reactions.

Among the considered DFT methods, hybrid functionals based on PBEPBE display the widest range of applicability for a given amount of exact exchange. In particular, PBE1PBE (25% of exact exchange) provides accurate results for the energy barriers and reaction energies of both reactions.

Finally, we have computed the error relative to CBS-QB3 obtained with different methods for selected points along the IRC corresponding to the second step of the two reactions. In general, the errors tend to increase as we approach the transition state. Density functionals with the largest amount of exact exchange (BHandHLYP, BB1K, and M05-X) and PBE1PBE are the ones to provide the best results for reaction paths before the transition state.

Supporting Information Available: Total energies and Cartesian coordinates of all structures used in this study, potential energy barriers at different stages of the CBS-QB3 calculation for the S_N2 reactions, and IRC graphics of reactions of sulfur ylide with formaldehyde and 1,1-dicianoethylene. This information is available free of charge via the Internet at http://pubs.acs.org.

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